

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Stabilized Vinyl Chloride Polymers

We, METAL & THERMIT CORPORATION, a Corporation organised under the Laws of the State of New Jersey, of Rahway, New Jersey, United States of America, (Assignees of Elliott Lawrence Weinberg) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is based on our discovery that mercaptal and mercaptol derivatives of mercaptoacid esters, mercaptans and mercaptoalkanol esters are effective to stabilise against the deleterious effects of heat homopolymers of vinyl chloride and copolymers of a major proportion of vinyl chloride and a minor proportion of vinyl acetate.

It has been found that the effectiveness of the above-mentioned mercaptal and mercaptol derivatives as stabilisers for the aforesaid polymers may be increased remarkably when used in conjunction with a small amount of secondary stabiliser.

Mercaptal and mercaptol derivatives of mercaptoacid esters, mercaptans and mercaptoalkanol esters of the formula



are particularly effective stabilizers for the aforesaid polymers. In this formula R and R¹ may be the same or different and represent substituted or unsubstituted alkyl, aryl or aralkyl groups. Typical examples are: propyl, 2-ethylhexyl, phenyl, stearyl, methyl, ethyl, tolyl, anisyl, benzyl, p-amylphenyl, and phenylethyl groups. R¹ may also be hydrogen. When SR¹¹ is the residue of a mercaptan, R¹¹ is also a substituted or unsubstituted alkyl, aryl or aralkyl group.

When SR¹¹ is the residue of a mercaptoacid ester, R¹¹ has the formula R¹¹¹COOR¹¹¹, wherein R¹¹¹ is linked to the sulphur and is a substituted or unsubstituted alkylene, aralkylene or arylene group, e.g., a methylene, ethylene, 2-carboxylethylene, 2-carboxy

phenylene, 2-alkylcarboxyethylene, 2-arylcarboxyethylene, or phenylene group; and R¹¹¹ is a substituted or unsubstituted alkyl, aryl or aralkyl group. When SR¹¹ is the residue of a mercapto-alkanol ester, R¹¹ has the formula —R¹¹¹OOCR¹¹¹, wherein R¹¹¹ is linked to the sulphur and R¹¹¹ and R¹¹¹ are defined as in the preceding sentence.

Among the mercaptal derivatives of mercaptoacid esters that are useful in the practice of the present invention may be mentioned the mercaptals of benzaldehyde with nonyl mercaptoacetate, 2-ethyl hexaldehyde with nonyl mercaptoacetate, benzaldehyde with isooctyl mercaptoacetate, benzaldehyde with decyl mercaptoacetate, 2-ethyl hexaldehyde with decyl mercaptoacetate, benzaldehyde with dodecyl mercaptoacetate, 2-ethyl hexaldehyde with dodecyl mercaptoacetate, benzaldehyde with nonyl β mercaptopropionate, 2-ethyl hexaldehyde with nonyl β mercaptopropionate and phenylethylaldehyde with nonylmercaptoacetate.

Included among the mercaptol derivatives of mercaptans that are useful in the present invention are mercaptol derivatives of benzophenone with ethyl mercaptan, benzophenone with lauryl mercaptan, methyl isobutyl ketone with ethyl mercaptan, methyl isobutyl ketone with lauryl mercaptan, benzophenone with thiophenol, isobutyl ketone with thiophenol, methyl isobutyl ketone with benzyl mercaptan, dibenzyl ketone with ethyl mercaptan, dibenzyl ketone with lauryl mercaptan.

The mercaptol derivatives of mercaptoacid esters that are useful stabilizers in the practice of this invention include the mercaptol derivatives of benzophenone with nonyl mercaptoacetate, methyl isobutyl ketone with nonyl mercaptoacetate, benzophenone with isooctylmercaptoacetate, methyl isobutyl ketone with isooctyl mercaptoacetate, dibenzyl ketone with nonyl mer-

captoacetate and dibenzyl ketone with iso-octyl mercaptoacetate.

Among the mercaptol derivatives of the mercaptoalkanol esters useful in the present invention are the mercaptal derivatives of benzaldehyde with the mercaptoethanol ester of acetic acid ($\text{SH}-\text{CH}_2-\text{CH}_2\text{OOCCH}_3$), benzaldehyde with the mercaptopropanol ester of acetic acid ($\text{SH}-\text{CH}_2\text{CH}_2-\text{CH}_2\text{OOCCH}_3$), 2-ethyl hexaldehyde with the mercaptoethanol ester of acetic acid, benzaldehyde with the mercaptoethanol ester of benzoic acid ($\text{SH}-\text{CH}_2-\text{CH}_2\text{OOCCH}_2\text{C}_6\text{H}_5$) and 2-ethyl hexaldehyde with the mercaptoethanol ester of benzoic acid. The mercaptol derivatives of the mercaptoalkanol esters of this invention include the mercaptol derivative of benzophenone with the mercaptoethanol ester of acetic acid, methyl isopropyl ketone with the mercaptoethanol esters of acetic acid, benzophenone with the mercaptoethanol ester of benzoic acid, methyl isopropyl ketone with the mercaptoethanol ester of benzoic acid, and dibenzyl ketone with the mercaptoethanol ester of phenyl acetic acid ($\text{SH}-\text{CH}_2\text{CH}_2-\text{OOCCH}_2-\text{C}_6\text{H}_5$).

The mercaptal and mercaptol derivatives are effective as stabilizers in amounts as low as 1% by weight (based on the weight of the polymer). It is not contemplated that more than about 5% should be incorporated in the polymer. Preferably from 1-5% is used.

Secondary stabilizers which may be used with mercaptal and mercaptol derivatives of mercaptoacid esters, mercaptans and mercaptoalkanol esters include organotin stabilizers and antimony compounds. The organotin stabilizers are the organotin derivatives of oxycompounds, i.e., derivatives of carboxylic acids, aldehydes, ketones, alcohols, phenols, hydroxy acids and tin oxide ester reaction products. Specific examples include dimethyl tin oxide, dilauryl tin oxide, dibutyl tin oxide, dibutyl tin-dilauryl, dibutyl tin maleate, butyl stannic acid and the reaction product of dibutyl tin oxide and 2-ethyl hexanal.

The antimony compounds useful as secondary stabilizers in this invention are the trialkyl and triaryl antimonites, antimony compounds, antimony oxychloride and antimony trioxide. Specific examples include tributyl antimonite, triphenyl antimonite, antimony octoate, antimony acetate, and antimonyl phthalate.

When utilizing a two stabilizer system, in accord with the present invention, the secondary stabilizer is used in amounts between 0.05 and 1.5% by weight (based on weight of the polymer) and preferably between 0.05 and 0.20%. The secondary stabilizer is used in conjunction with the primary stabilizer which is present in amounts between 1 and 5% by weight and preferably between 1 and 2½% (based on weight of polymer).

The mercaptal and mercaptol derivatives are relatively inexpensive compounds. Their stabilizing effectiveness is greatly improved when using small amounts of a secondary stabilizer or stabilizers. The two system stabilizer is comparative in effectiveness with equivalent amounts of organic metallic stabilizers which are far more expensive. Thus, in the case where the aforementioned organotin compounds are used in conjunction with the primary stabilizers, the same stabilizing effect is obtained as when much larger quantities of the expensive organotin compound are used alone.

The following examples are further illustrative of the invention.

The polymer used in Examples 1-16 was a homopolymer of polyvinyl chloride. The polymer used in Examples 17-24 was a vinyl chloride vinyl acetate copolymer resin (VYNW-5) containing a major portion of vinyl chloride and a minor portion of vinyl acetate.

EXAMPLES.

The mercaptal and mercaptol derivatives of the mercaptoacid esters, mercaptans and mercaptoalkanol esters are made by standard synthesis. Thus, in Example No. 11, the mercaptal of benzaldehyde and nonyl mercaptoacetate was prepared by heating 1 part of benzaldehyde with two parts of nonyl mercaptoacetate, in the presence of a small amount of concentrated sulphuric acid, on a steam bath for 16 hours.

The stabilizers were tested by incorporating them in the above noted resins. In each example, except Example IV, the stabilizer (or a mixture of the primary stabilizer with a secondary stabilizer) was incorporated into a test mixture consisting of 100 parts by weight of the polymer just specified and 50 parts by weight of dioctyl phthalate plasticizer. In the case of Example IV, as noted below, the plasticizer was of different composition. The amount of stabilizer (specified in parts by weight) is that incorporated in 150 parts of the test mixture. The mixture was milled for 5 minutes on a two-roll differential speed mill heated to 320° to 325° F. The mill sheet was cut into 1" by 6" strips and placed on a glass sheet in a tray. The tray was then placed in a circulating air oven held at 350° F. Samples were removed after an hour and a quarter and rated visually.

EXAMPLE I.

A test plasticized resin mixture containing no stabilizer was tested. After 1½ hours, the sheet (transparent when the test started) was black and totally opaque.

EXAMPLE II.

One part of the mercaptal of benzaldehyde and nonyl mercaptoacetate and 0.1 part of antimony trioxide were incorporated into

a test mixture. At the end of 1½ hours the test specimen was a very light yellow.

EXAMPLE III.

Two parts of the mercaptal of benzaldehyde and nonyl mercaptoacetate and 0.5 parts of dibutyltin dilaurate were incorporated into a test mixture. At the end of 1½ hours the test specimen was yellow.

EXAMPLE IV.

One part of the mercaptal of 2-ethylhexaldehyde and nonyl mercaptoacetate and 0.1 part of dibutyltin maleate were incorporated into a test mixture containing 100 parts of a polyvinyl chloride homopolymer, 35 parts of dioctyl phthalate and 15 parts of tricresylphosphate. At the end of 1½ hours, the test specimen was a light amber.

EXAMPLE V.

One part of the mercaptal of 2-ethylhexaldehyde and nonyl mercaptoacetate and 0.5 parts of dibutyl maleate were incorporated into a test mixture. At the end of 1½ hours the test specimen was yellow.

EXAMPLE VI.

Two parts of the mercaptal of 2-ethylhexaldehyde and nonyl mercaptoacetate and 0.1 part of antimony trioxide were incorporated into a test mixture. At the end of 1½ hours the test specimen was colorless.

EXAMPLE VII.

Two parts of the mercaptal of benzaldehyde and nonyl mercaptoacetate and 1 part of dibutyltin oxide were incorporated into a test mixture. At the end of 1½ hours the test specimen was colorless.

EXAMPLE VIII.

Two parts of the mercaptal of benzaldehyde and isooctyl mercaptoacetate and 0.5 parts of dibutyltin oxide were incorporated into a test mixture. At the end of 1½ hours the test specimen was colorless.

EXAMPLE IX.

Two parts of the mercaptal of benzaldehyde and isooctyl mercaptoacetate and 0.5 parts of dibutyltin dilaurate were incorporated into a test mixture. At the end of 1½ hours the test specimen was colorless.

EXAMPLE X.

Two parts of the mercaptal of benzaldehyde and isooctyl mercaptoacetate were incorporated into a test mixture. At the end of 1½ hours the test specimen was amber.

EXAMPLE XI.

Two parts of the benzophenone mercaptol of isooctyl mercaptoacetate and 0.1 part of antimony trioxide were incorporated into a

test mixture. At the end of 1½ hours the test specimen was amber.

EXAMPLE XII.

Two parts of the benzophenone mercaptol of isooctyl mercaptoacetate and 0.5 parts of antimony oxychloride were incorporated into a test mixture. At the end of 1½ hours the test specimen was amber.

EXAMPLE XIII.

Two parts of the benzophenone mercaptol of isooctyl mercaptoacetate were incorporated into a test mixture. At the end of 1½ hours the test specimen was amber.

EXAMPLE XIV.

Two parts of the methyl isobutyl ketone mercaptol of isooctyl mercaptoacetate were incorporated into a test mixture. At the end of 1½ hours the test specimen was amber.

EXAMPLE XV.

Two parts of the methyl isobutyl ketone mercaptol of isooctyl mercaptoacetate and 0.5 parts of antimony oxychloride were incorporated into a test mixture. At the end of 1½ hours the test specimen was yellow.

EXAMPLE XVI.

Two parts of the methyl isobutyl ketone mercaptol of isooctyl mercaptoacetate and 0.1 part of antimony oxide were incorporated into a test mixture. At the end of 1½ hours the test specimen was a light yellow.

EXAMPLE XVII.

A mixture that did not contain a stabilizer was tested. After 1 hour, the sheet (transparent when the test started) was black and opaque.

EXAMPLE XVIII.

Two parts of mercaptal of benzaldehyde and isooctyl mercaptoacetate were incorporated into a test mixture. At the end of 1 hour the test specimen was amber.

EXAMPLE XIX.

Two parts of the methyl isobutyl ketone mercaptol of isooctyl mercaptoacetate were incorporated into a test mixture. At the end of 1 hour the test specimen was amber.

EXAMPLE XX.

Two parts of the methyl isobutyl ketone mercaptol of isooctyl mercaptoacetate and 0.1 part of antimony oxide were incorporated into a test mixture. At the end of 1 hour the test specimen was a light yellow.

EXAMPLE XXI.

Two parts of the methyl isobutyl ketone mercaptol of isooctyl mercaptoacetate and 0.5 parts of antimony oxychloride were in-

corporated into a test mixture. At the end of 1 hour the test specimen was a light yellow.

EXAMPLE XXII.

- 5 Two parts of the benzophenone mercaptol of isoocyl mercaptoacetate and 0.5 part of antimony oxychloride were incorporated into a test mixture. At the end of 1 hour the test specimen was very light yellow.

10 EXAMPLE XXIII.

Two parts of the benzophenone mercaptol of isoocyl mercaptoacetate were incorporated into a test mixture. At the end of 1 hour the test specimen was amber.

15 EXAMPLE XXIV.

Two parts of the benzophenone mercaptol of isoocyl mercaptoacetate and 0.1 part of antimony trioxide were incorporated into a test mixture. At the end of 1 hour the test specimen was a light yellow.

20 WHAT WE CLAIM IS:—

1. A homopolymer of vinyl chloride, or a copolymer of a major proportion of vinyl chloride and a minor proportion of vinyl acetate, containing, as a stabilizer against the deleterious effect of heat, a mercaptal or mercaptol derivative of a mercaptan, a mercaptoacid ester or a mercaptoalkanol ester.

2. A composition according to Claim 1, in which the stabiliser is a compound of the formula $RR^1C(SR^{II})_2$, and in which R is a substituted or unsubstituted alkyl, aryl or aralkyl radical, R^1 is a hydrogen atom or a substituted or unsubstituted alkyl, aryl or aralkyl radical and SR^{II} is the residue of a mercaptan, a mercaptoacid ester or a mercaptoalkanol ester.

3. A composition according to Claim 1 or Claim 2, which includes as a secondary stabilizer an organotin compound or an antimony compound, or a mixture of an organotin compound and an antimony compound.

4. A composition according to Claim 3, in which the secondary stabiliser is a hydrocarbontin oxy-compound or an antimony oxy-compound.

5. A composition according to Claim 4, in which the secondary stabilizer is a hydrocarbontin oxide, a hydrocarbon stannic acid, a hydrocarbontin derivative of a carboxylic acid, an aldehyde, a ketone, an alcohol, a phenol or a hydroxy acid, a tin oxide ester reaction product, a trialkyl antimonite, a triaryl antimonite, an antimonyl compound of a carboxylic acid, antimony oxychloride or antimony trioxide.

6. A composition according to Claim 1 or Claim 2, in which the stabilizer is present within the range of 1 to 5% by weight, based on the weight of the polymer.

7. A composition according to Claim 4, in which the main stabilizer is present within the range of 1—5% by weight based on the weight of the polymer and the secondary stabilizer is present within the range of 0.05—1.5% by weight based on the weight of the polymer.

8. A composition according to Claim 4, in which the main stabilizer is present within the range of 1—2½% by weight based on the weight of the polymer and the secondary stabilizer is present within the range of 0.05—0.2% by weight based on the weight of the polymer.

9. A composition according to Claim 1, in which the stabilizer is constituted by a compound of formula $RR^1C(SR^{II}OOCR^{III})_2$, wherein R is a substituted or unsubstituted alkyl, aryl or aralkyl radical, R^1 is a substituted or unsubstituted alkyl, aryl or aralkyl radical or a hydrogen atom R^{II} is a substituted or unsubstituted alkylene, arylene or aralkylene radical and R^{III} is a substituted or unsubstituted alkyl, aryl or aralkyl radical.

10. A composition according to Claim 2, in which the stabilizer is the substance disclosed in any of the foregoing examples.

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